In (B1) the value of λ from eq 13b is used. After some algebra we obtain

$$\frac{d\tilde{\mu}_0}{d\tilde{T}} = \frac{3}{2s\tilde{T}} + \frac{\frac{q}{2}[\epsilon\beta_c + 2\beta_c\phi t_2]}{s\left[1 + \frac{q}{2}(t_2 - t_0)\right]} \quad \text{(B2)}$$

Here

$$t_n = \frac{z_A\eta_A{}^n}{1 + z_A\eta_A{}^n} \quad (n = 0, 1, 2) \quad \text{(B3)}$$

At the critical point, eq B2 becomes the lattice gas analogue of the parameter $\tilde{\mu}_1$ (eq 24) of the scaled equation.

The mixing parameter c of the fluid (eq 23), which indicates the strength of the contribution of the chemical potential in the definition of the temperature-like scaling field, also has a lattice gas analogue. This becomes evident by comparing eq 13c for the temperature-like scaling field of the Mermin model with eq 8c for the simple lattice gas and noting that (13c) contains the activity as well as the temperature. From the definition of the mixing parameter (eq 23) we find, for the decorated lattice gas

$$\bar{c} = \frac{(\partial\zeta/\partial\bar{\mu})_{\tilde{T}}}{(\partial\zeta/\partial\tilde{T})_{\bar{\mu}}} \quad \text{(B4)}$$

where (13c) is used for ζ. After some algebra we obtain

$$\bar{c} = s\left[\frac{\beta_c\phi(t_2{}^c - t_1{}^c) + \epsilon\beta_c/2}{t_1{}^c - (t_0{}^c + t_2{}^c)/2} + \frac{3}{2} + s\bar{\mu}_1\right]^{-1} \quad \text{(B5)}$$

In (B5) $t_n{}^c$ denotes the quantity defined in (B3) evaluated at the solvent critical point.

Electrical Conductivity, Viscosity, and Density of a Two-Component Ionic System at Its Critical Point

Donald R. Schreiber, M. Conceicao P. de Lima,† and Kenneth S. Pitzer*

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 *(Received: November 14, 1986)*

The density, viscosity, and electrical conductivity of a system composed of a fused salt in a low dielectric constant solvent were examined at a temperature just above the liquid–liquid critical point. The system examined was tetra-*n*-butylammonium picrate (TNBAP) in 1-chloroheptane. The conductivity decreased to a minimum near 0.001 mol/dm^3 and then increased rapidly through the region of the critical concentration. The data in the region of the minimum were fit by using the method of Fuoss and Kraus to determine the ion-pair and ion-triplet dissociation constants. An extrapolation of these equilibria toward the critical region indicated a rapidly increasing importance of ion triplets at the expense of the neutral ion pairs. The conductivity results were also compared to a recent cluster-equilibrium treatment of the restrictive primitive model (RPM). This treatment of the RPM also shows an increasing importance of charged clusters, at the expense of neutral clusters, as the concentration approaches that of the critical point. The dielectric constant of 1-chloroheptane was also measured over a range of temperature.

Introduction

While the region of the liquid–liquid critical point for partially miscible mixtures has been extensively studied for systems of neutral molecules,[1] little is known about ionic systems at their critical points. Recently we reported the liquid–liquid phase diagram including the critical point for the tetra-*n*-butylammonium picrate (TNBAP)–1-chloroheptane system (T_c = 414.4 K, x_c = 0.085, c_c = 0.43 mol/dm^3).[2] This system presented us with an opportunity to examine for the first time several other properties of a two-component ionic system near its critical point. In this paper we present the results of an examination of the electrical conductivity, viscosity, and density of this system. Values are reported over a range of concentrations, including the critical composition, at a temperature just above the critical point and at a somewhat higher temperature. The dielectric constant of 1-chloroheptane was also measured as it was not available at elevated temperatures.

Mixtures of neutral-molecule liquids in the region of their critical points have been investigated and it was found that the shape of the two-phase curve deviates from that predicted by classical theory. Similiar deviations have been seen in nonionic liquid–vapor and magnetic systems. These systems are characterized by fluctuations in composition, density, or magnetism that become nearly macroscopic as the critical point is approached.[3] The deviation from classical theory occurs when the range of these fluctuations becomes longer than the range of interparticle interactions. Modern critical point theory takes into account these fluctuations and can therefore account for the shape of the phase separation curve in the region of a critical point.[3] A recent review[4] discusses these characteristics of the two-phase curves as well as certain other properties showing anomalous behavior near the critical point. Unlike the results seen with neutral molecules, our earlier results indicated classical behavior for the ionic system. These results suggested that the interparticle forces for the TNBAP–chloroheptane system near its critical point were of much longer range than those for typical neutral molecules. This conclusion seems reasonable since ionic forces are longer range ($1/r$) than those of neutral molecules ($1/r^6$).

In an attempt to determine the nature of the solution in the region of the critical point, the electrical conductivity, viscosity, and density were examined. The conductivity of a solution is dependent on the concentration and mobility of the ions present in solution. Reduction of the number of ions present via formation of neutral ion pairs has been shown to reduce the equivalent conductance.[5,6] Previous studies[7,8] have shown that TNBAP forms

† Permanent address: Department of Chemistry, University of Coimbra, 300 Coimbra, Portugal.

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ion pairs at low concentrations in other low dielectric constant solvents. If a major proportion of the salt were ion-paired in the critical region it would modify the long-range nature of the interparticle forces. The density and viscosity data were used in the analysis of the conductivity.

Anomalous viscosity has been observed very close to the critical point for certain systems.[9,10] Our present measurements of viscosity do not show any anomaly, but they were intended merely to assist in the interpretation of the conductance data. More precise measurements at temperatures closer to the critical point are needed to explore for a viscosity anomaly in this ionic system.

Experimental Section

Tetra-*n*-butylammonium picrate (TNBAP) was prepared by neutralizing tetra-*n*-butylammonium hydroxide with picric acid. TNBAP was purified by recrystallization from ethanol and dried in a vacuum desiccator. 1-Chloroheptane (99.8%) was obtained from Aldrich Chemical Co. and used without further purification.

The densities of the salt solutions were measured by adding weighed amounts (±0.1 mg) of the components to a graduated glass cell fitted with a Teflon stopcock. Two Teflon-coated stirring bars were placed in the cell to ensure thorough mixing of the components. The sample was then degassed and the cell placed into an oil bath at 416.15 K. After the cell had equilibrated and the solution was one clear phase (1–2 h), the volume (±0.02 cm^3) of the solution was recorded. The volumes and weights were then used to calculate the densities of the solutions. The volume of the cell was determined by using decane[11] with the same magnetic stirring bars. Densities were measured over the entire mole fraction range. The experiments were repeated at 433.15 K to obtain the temperature coefficient.

The viscosity experiments were conducted by using a Gilmont falling ball viscometer. Once calibrated, the viscosity of the solution is determined by measuring the time for a ball to fall a prescribed distance in the tube. Equation 1 is used to relate the falling time of a given ball to the viscosity of the solution. In

$$\eta = k_v(\rho_b - \rho_s)t \quad (1)$$

eq 1 η is the viscosity of the solution, ρ_b the density of the ball, ρ_s the density of the solution, t the falling time, and k_v the viscometer constant. The viscometer was calibrated with glycerol by using the densities and viscosities reported by Miner and Dalton.[12] The solutions for the viscosity experiments were prepared by adding weighed amounts of TNBAP and chloroheptane to the tube and evacuating at room temperature. The tube was then placed in the bath up to its cap and allowed to equilibrate. The cap was loosened to allow any air bubbles to escape and retightened, and then the tube was completely submerged. The tube was inverted several times to ensure thorough mixing of the sample. Three falling times were then recorded and averaged. Due to the slight loss of sample that occurs when the air bubbles are allowed to escape, the composition of the solution must be redetermined. This was accomplished by removing a milliliter of solution from the cell and placing it into a vessel. The vessel was weighed, placed in a vacuum desiccator, and evacuated to remove the solvent. After removal of the solvent, the vessel was reweighed to determine the amount of chloroheptane present in the sample. After the TNBAP was removed from the vessel by rinsing with alcohol, the vessel was dried and weighed to determine the weight of picrate in the sample. The composition of the sample was then calculated by using these weights. The viscosity experiments were made at 416.15 and 433.15 K to determine the temperature coefficient.

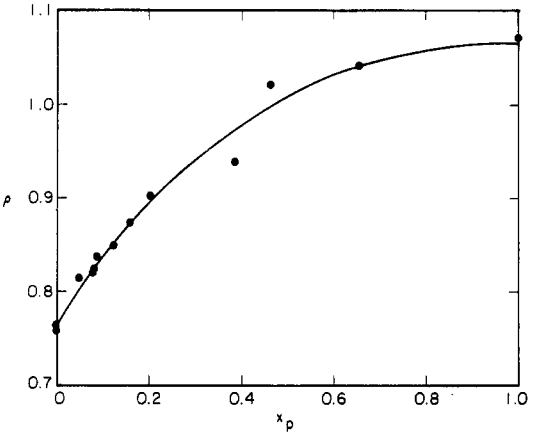

Figure 1. Plot of density (g/cm^3) vs. concentration (x_p) for the TNBAP–1-chloroheptane system at 416.15 K. The curve is the fit of eq 3 to the data.

A glass cell with separate mixing and measuring chambers was used for the conductivity experiments. The tops of the two chambers were connected by a small hollow glass bridge. To permit evacuation of the cell, a Teflon valve was attached to the sample inlet of the cell. The measuring chamber contained two parallel platinum electrodes attached to platinum leads. These leads were attached to tungsten wire that formed a vacuum-tight seal with the glass. The sample was prepared by adding weighed amounts of salt and chloroheptane to the mixing chamber. A small Teflon-coated magnetic stirring bar was placed in the mixing chamber and the cell was then evacuated. A magnetic stirrer underneath the bath was used to stir the sample. The cell was placed in an oil bath at 416.15 K, making sure the sample remained in the mixing chamber. Experiments were also performed at 433.15 K to obtain the temperature coefficient of the conductivity. After the solution had equilibrated at the experimental temperature (one phase), the sample was tipped into the measuring cell. When the temperature had once again stabilized, the leads from the cell were attached to a Wayne Kerr Model 6425 Precision Component Analyzer. The cell was calibrated by using aqueous potassium chloride.[13]

The equivalent conductance of the solution was then calculated from the experimental absolute conductance by using eq 2, where

$$\Lambda = k_c L(1000/c) \quad (2)$$

Λ is the equivalent conductance, L the observed conductance, c the concentration in mol/dm^3, and k_c the cell constant.

Results and Discussion

The density data (g/cm^3) at 416.15 K are plotted in Figure 1. The value for pure picrate was taken from Walden and Birr.[14] Equation 3 was fitted to the experimental data: ρ_s is the density

$$\rho_s = \rho_0 + p_1 x_p + p_2 x_p^{3/2} \quad (3)$$

of sample, ρ_0 the density of pure 1-chloroheptane (0.760_5 g/cm^3), and x_p the mole fraction of picrate salt. The $x_p^{3/2}$ term in eq 3 accounts for the variation of the apparent molar volume with concentration. The resulting coefficients and standard deviation of the fit for 416.15 K are $p_1 = 0.962$ g/cm^3, $p_2 = -0.656$ g/cm^3, and $\sigma = 0.015$ g/cm^3. For the measurements at 433.15 K, the density of pure chloroheptane is 0.751_5 g/cm^3 and coefficients and standard deviation are $p_1 = 1.143$ g/cm^3, $p_2 = -0.860$ g/cm^3, and $\sigma = 0.015$ g/cm^3. Equation 3 was used to calculate densities of the solutions used in the viscosity and conductivity experiments. The temperature coefficient of the density, based on measurements taken at 416.15 and 433.15 K, was -0.0005 g cm^{-3} K^{-1}. This

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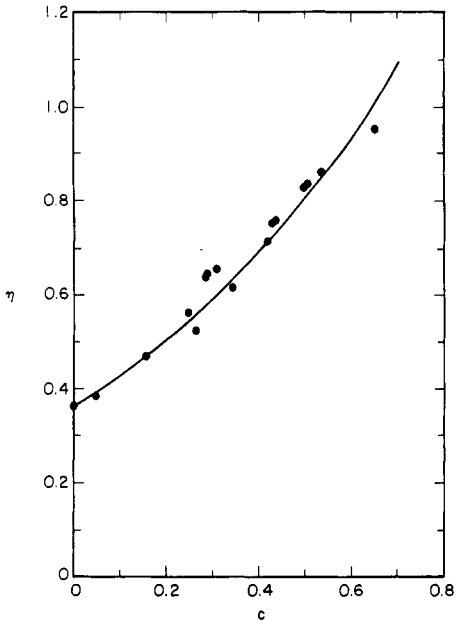

Figure 2. Plot of viscosity (cP) vs. concentration (mol/dm^3) for the TNBAP–1-chloroheptane system at 416.15 K. The curve is the fit of eq 4 to these data and the value of Walden and Birr[14] for pure TNBAP.

variation was within the uncertainty of the measurements (±2%) and should be regarded as approximate.

Figure 2 shows the results of the viscosity experiments at 416.15 K in centipoise where 1 cP equals 10^{-3} N s m^{-2}. Although the viscosity data show no anomalously high values in the region of the critical point, the uncertainty in the viscosity measurements (±10%) was quite large. This imprecision is large enough to mask an anomaly of the size seen in other systems[9,10] at a temperature of 2 K from the critical point. Experiments are continuing in an attempt to determine if a significant viscosity anomaly occurs very close to the critical point. Equation 4 was fit to these data and the value for pure picrate from Walden and Birr[14] (11.5 cP at 416.15 K; 7.82 cP at 433.15 K)). In eq 4 η is the viscosity of

$$\eta/\eta_0 = p_3 c^{1/2} + \exp(p_4 c) \qquad (4)$$

sample, η_0 the viscosity of pure 1-chloroheptane, and c the molar concentration (mol/dm^3). The resulting coefficients and standard deviation of the fit for 416.15 K are $p_3 = 0.196$, $p_4 = 1.51$, and $\sigma = 0.033$ with $\eta_0 = 0.361$ cP. For 433.15 K the curve is very similar. The viscosity of pure chloroheptane is 0.280 cP while the coefficients and standard deviation are $p_3 = 0.218$, $p_4 = 1.47$, and $\sigma = 0.024$. This form of equation was chosen because it combines the dependence seen at both low ($c^{1/2}$) and high concentrations ($\exp(c)$).[15]

There is a substantial range from the highest concentration of measurement to the pure picrate over which eq 4 is an interpolation and subject to considerable uncertainty. The temperature coefficient of the viscosity varied from −0.0048 cP/K for pure chloroheptane to −0.22 cP/K for pure picrate.[14]

The results of the conductivity experiments at 416.15 K are listed in Table I and shown in Figure 3. Also shown is the conductance–viscosity or Walden product which is more nearly indicative of the ion concentration than the conductance itself. Both the Λ and $\Lambda\eta$ curves show a minimum near $c = 0.001$ mol/dm^3 followed by a rapid increase with concentration. The minimum is attributable to the initial formation of ion pairs with subsequent formation of triple ions. At higher concentration the value of $\Lambda\eta$ increases smoothly to that of the pure picrate. The conductance itself, however, shows a maximum and a decrease at high concentration which can be attributed to a rapid increase in viscosity. In the region of the critical composition both Λ and $\Lambda\eta$ are smooth and rapidly increasing.

In the dilute range, the conductance results are of particular interest for the information they give concerning the distribution among single ions, ion pairs, larger neutral clusters, and charged clusters. Eventually this speciation ceases to have meaning at high

TABLE I: Equivalent Conductivity and Conductivity–Viscosity Product Data for the Tetra-*n*-butylammonium Picrate–1-Chloroheptane System at 416.15 K

mole fraction	concn, mol/dm^3	Λ	$\Lambda\eta$
6.45×10^{-6}	3.65×10^{-5}	1.91	2.41×10^{-3}
1.08×10^{-5}	6.10×10^{-5}	1.27	4.59×10^{-3}
2.77×10^{-5}	1.57×10^{-4}	1.16	4.20×10^{-3}
4.04×10^{-5}	2.28×10^{-4}	0.875	3.17×10^{-3}
5.52×10^{-5}	3.12×10^{-4}	0.715	2.59×10^{-3}
5.92×10^{-5}	3.35×10^{-4}	0.676	2.45×10^{-3}
9.90×10^{-4}	5.59×10^{-4}	0.663	2.41×10^{-3}
1.42×10^{-4}	8.02×10^{-4}	0.545	1.98×10^{-3}
1.83×10^{-4}	1.03×10^{-3}	0.437	1.59×10^{-3}
3.06×10^{-4}	1.73×10^{-3}	0.510	1.86×10^{-3}
3.06×10^{-4}	1.73×10^{-3}	0.490	1.79×10^{-3}
7.98×10^{-4}	4.50×10^{-3}	0.475	1.75×10^{-3}
9.20×10^{-4}	5.19×10^{-3}	0.444	1.64×10^{-3}
$2.21_5 \times 10^{-3}$	1.25×10^{-2}	0.562	2.11×10^{-3}
2.99×10^{-3}	1.68×10^{-2}	0.883	3.35×10^{-3}
3.96×10^{-3}	2.22×10^{-2}	0.901	3.46×10^{-3}
5.53×10^{-3}	3.10×10^{-2}	1.16	4.55×10^{-3}
8.99×10^{-3}	5.02×10^{-2}	1.78	7.21×10^{-3}
1.65×10^{-2}	9.12×10^{-2}	3.62	1.58×10^{-2}
2.55×10^{-2}	1.39×10^{-1}	3.99	1.88×10^{-2}
2.63×10^{-2}	1.44×10^{-1}	4.09	1.95×10^{-2}
3.44×10^{-2}	1.86×10^{-1}	5.75	2.92×10^{-2}
$3.72_1 \times 10^{-2}$	2.00×10^{-1}	4.90	2.55×10^{-2}
$4.63_6 \times 10^{-2}$	2.00×10^{-1}	5.10	2.85×10^{-2}
4.98×10^{-2}	2.64×10^{-1}	5.58	3.20×10^{-2}
5.824×10^{-2}	3.05×10^{-1}	6.73	4.12×10^{-2}
6.593×10^{-2}	3.42×10^{-1}	6.69	4.33×10^{-2}
8.495×10^{-2}	4.30×10^{-1}	8.00	5.90×10^{-2}
8.761×10^{-2}	4.42×10^{-1}	8.72	6.55×10^{-2}
1.035×10^{-1}	5.12×10^{-1}	8.74	7.28×10^{-2}
1.256×10^{-1}	6.05×10^{-1}	10.0	9.56×10^{-2}
1.494×10^{-1}	7.00×10^{-1}	10.6	1.17×10^{-1}
1.910×10^{-1}	8.54×10^{-1}	10.28	1.42×10^{-1}
3.037×10^{-1}	1.21	8.33	1.94×10^{-1}
3.778×10^{-1}	1.40	7.04	2.18×10^{-1}
7.594×10^{-1}	2.06	4.96	4.08×10^{-1}
1.0	2.278	3.69	4.24×10^{-1}

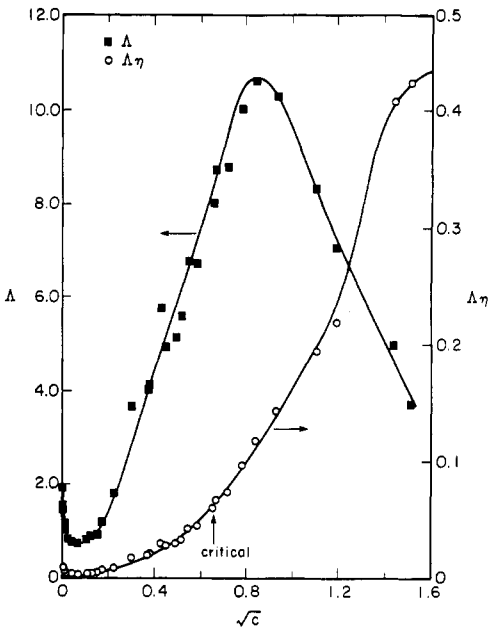

Figure 3. Plot of the conductivity (■) and the conductance–viscosity product (○) for the TNBAP–1-chloroheptane system vs. concentration (mol/dm^3) at 416.15 K. Smooth curves have been drawn through the data for presentation purposes.

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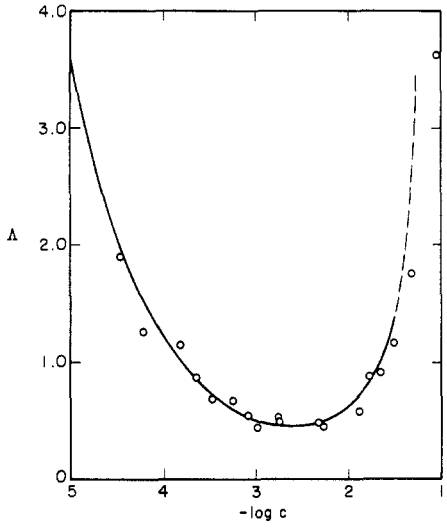

Figure 4. Plot of the fit of the low concentration conductivity data using the method of Fuoss and Kraus.[5,6]

concentration where the structural pattern becomes that of a fused salt with a disordered lattice of alternating charges. The critical concentration lies in a transition range where a speciation treatment is no longer valid yet the system is substantially expanded from a typical fused salt. We present two treatments for the dilute or vaporlike region where cluster speciation is meaningful (Figure 4).

We first apply the method of Fuoss and Kraus[5] who assumed association equilibria to ion pairs and to triple ions and included the approximate Debye–Hückel and Onsager's corrections for activity coefficients and conductance. We have used the extended form for these corrections suggested by Robinson and Stokes.[6] This was accomplished by using eq 5, where Λ is the equivalent

$$\Lambda c^{1/2} g = \Lambda_0 K^{1/2} + \lambda_0 K^{1/2} c(1 - \Lambda/\Lambda_0)/k \qquad (5)$$

conductance, Λ_0 the limiting conductance of the single ion, λ_0 the limiting conductance of the ion triplet, c the concentration in mol/dm^3, K the dissociation constant for the ion pair, and k the dissociation constant for the ion triplet. The coefficient g accounts for the change with concentration of the activity and mobility of the ions and is given[6] by eq 6 where α is Onsager's coefficient,

$$g = \exp\left\{\frac{-\beta(c\Lambda/\Lambda_0)^{1/2}}{(1 + Ba(c\Lambda/\Lambda_0)^{1/2})}\right\} \Bigg/ \left[\left\{1 - \alpha\Lambda_0^{-3/2}\left[\frac{(c\Lambda)^{1/2}}{(1 + Ba(c\Lambda/\Lambda_0)^{1/2})}\right]\right\}(1 - (\Lambda/\Lambda_0))^{1/2}\right] \qquad (6)$$

β the Debye–Hückel parameter, and B the coefficient of the ion size parameter, a, which was taken to be 7 Å.[16]

The limiting conductance of the single ion was allowed to vary in order to obtain the best fit. The values $\Lambda_0 = 123$ and $K = 9.2 \times 10^{-9}$ mol^{-1} dm^3 yield good agreement with the data up to 0.03 mol/dm^3. The Λ_0 may also be calculated by using Walden's rule which states that $\Lambda_0\eta_0$ for a given salt is constant for all solvents at a given temperature. The Λ_0 calculated from data for several solvents[7,8] by using Walden's rule, 120, is in good agreement with the value we obtained using the method of Fuoss and Kraus,[5] 123.

Equation 5 does not yield either the limiting conductance or the dissociation constant of the triple ion separately but only their ratio, $\lambda_0/k = 3.1 \times 10^4$. If one assumes the same limiting conductance for the single and triple ions, then $k = 4.0 \times 10^{-3}$ mol^{-1} dm^3 and one can calculate a speciation diagram over the concentration range to 0.03 mol/dm^3 (Figure 5). The speciation diagram shows that a rapid increase in triple ion population begins at a concentration below one-tenth that of the critical point.

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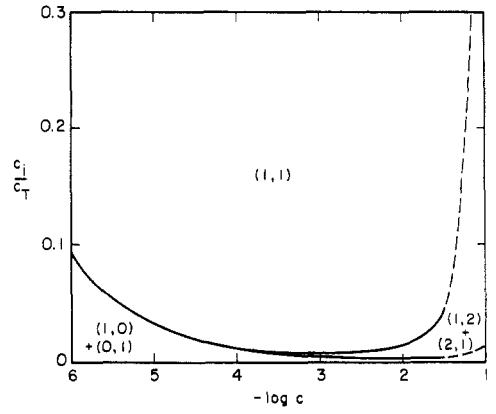

Figure 5. Speciation of TNBAP as a function of concentration (mol/dm^3) in 1-chloroheptane using the constants calculated with eq 5. The symbol c_T denotes the concentration of ions of the completely dissociated salt. The symbol (s,t) indicates the number of positive ions, s, and negative ions, t, for that cluster. The vertical distance between lines gives the fraction of particles in the particular type of cluster.

The conductivity at 433.15 K shows the same general pattern, but the temperature coefficient varies with concentration; hence, eq 5 was also fit to the 433.15 K conductivity data. The values $\Lambda_0 = 169$, $K = 4.4 \times 10^{-9}$ mol^{-1} dm^3, $\lambda_0 = 169$, and $k = 3.1 \times 10^{-3}$ mol^{-1} dm^3 were obtained by using the same assumptions as at 416.15 K. Any model based on ions in a continuous dielectric will have only limited validity for a system with a molecular solvent, but it is interesting to make comparisons. The effective temperature for any model of this type is the ϵT product which is essentially constant at 1600 K for 1-chloroheptane from 273 to 440 K. Thus, the appearance of the critical point is itself a departure from the simple model. Nonelectrostatic forces must play a significant role in this system. From the nature of these components, this conclusion is reasonable. Also, one cannot expect the ion-pair dissociation constant to be independent of temperature, and it does decrease from 9.2×10^{-9} mol^{-1} dm^3 at 416 K to 4.4×10^{-9} mol^{-1} dm^3 at 443 K. Such departures from the purely electrostatic model are known for other fused-salt–polar-solvent systems.[17,18]

The conductivity data can also be compared to the results of our recent calculations of cluster equilibria based on the restrictive primitive model (RPM).[19] The RPM has frequently been used by statistical mechanicians for modeling electrolyte solutions. The model assumes the ions are hard spheres immersed in a dielectric continuum. The potential between the ions ($u_{i,j}$) is

$$u_{i,j} = \infty \qquad \text{for } r < \sigma$$
$$= e^2 z_i z_j/(\epsilon r) \qquad \text{for } r > \sigma$$

where r is the distance between the ions, σ is the hard core diameter, e is the charge of an electron, z_i and z_j are the charges on the ions, and ϵ is the dielectric constant; also one has the inverse reduced temperature $\beta^* = z^2e^2/\epsilon kT\sigma$. For SI units the factor $4\pi\epsilon_0$ multiplies ϵ in each expression. In our treatment we included neutral and singly charged ionic clusters up to 6 particles. Particles separated by less than 2σ were taken as clustered. The intercluster interactions were calculated by using the mean spherical approximation. The free energy of the ion pair was first given by Bjerrum[20] while Gillan[21] calculated this property by Monte Carlo methods for the larger clusters.

There remains considerable uncertainty concerning the critical point of the RPM but it is almost certainly[19] within the range of 14–17 for β^*. Figure 6 shows our conductance data with alternate curves based on the RPM with β^* values of 14 and 17. All of the charged species were assumed to have the same limiting

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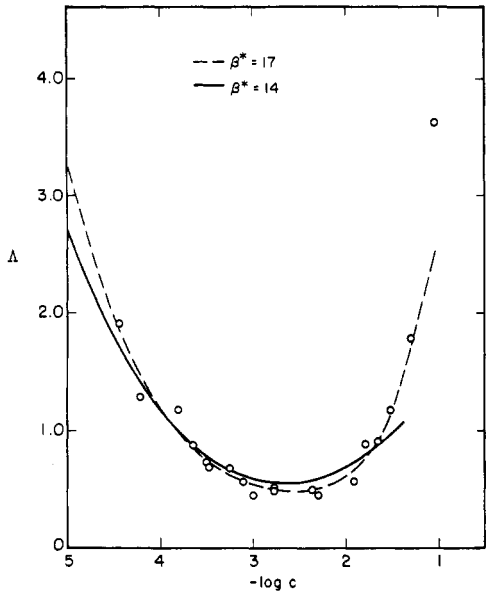

Figure 6. Comparison of conductivity data to predictions of the restrictive primitive model, for $\beta^* = 14$ (—) and $\beta^* = 17$ (---). The comparison assumes the same equivalent conductance for all charged species at all concentrations.

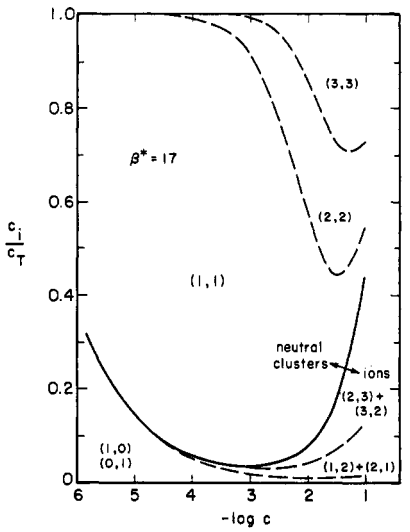

Figure 7. Speciation of RPM as a function of concentration (mol/dm³) at a temperature near the predicted critical point ($\beta^* = 17$). Additional details are the same as in Figure 5.

conductance. There are two adjustments in these comparisons. First is the assumed conductance per ion. Second is the relationship of the concentration scale of the RPM to that of the experimental system. Clearly the better fit is obtained for $\beta^* = 17$. In this case the $\Lambda_0 = 46$. The model concentrations were multiplied by a proportionality factor so that the concentration at the minimum of the experimental data and that of the model agreed. This is possible since the RPM scale (particles per unit volume) is proportional to the molar concentration scale. The proportionality factor used for comparison is related to the hard core diameter. The hard core diameter calculated by using the proportionality factor from the comparison of the RPM and molar concentration scales, 7.14 Å, agrees well with the value for TNBAP calculated by Pitzer and Simonson.[16] With this proportionality constant one obtains approximately the correct molar concentration for pure picrate at 416.15 K. Also with the proportionality constant we obtain a speciation diagram on a molar scale (Figure 7), which is limited in validity to a concentration of 0.09 mol/dm³. As shown by the speciation diagram, the fraction of ions is increasing with concentration above the conductance minimum and quintuple ions become important as well as triple ions.

TABLE II: Dielectric Constant of 1-Chloroheptane

T, K	ε	T, K	ε	T, K	ε
0.00	5.909[a]	50.31	4.87	119.97	4.00
10.00	5.713[a]	60.31	4.73	129.84	3.93
20.00	5.521[a]	70.06	4.60	140.01	3.80
30.00	5.270[a]	80.06	4.47	143.24	3.80
40.00	5.092[a]	90.15	4.40	154.42	3.73
50.00	4.921[a]	100.26	4.27	160.03	3.67
		110.18	4.13		

[a] From ref 24.

Despite the loss of quantitative validity of both the RPM and the Fuoss and Kraus models at the critical composition (0.43 mol/dm³), both models are qualitatively consistent with the rapid increase in conductivity as the critical composition is approached. The very substantial conductance at critical composition also agrees with our previous assumption that long-range forces are important near the critical point.

While the speciation models lose exact meaning as the concentration approaches that of the critical point, it is still of interest to note that both ion pairs and charged clusters are important in this region. Hence, the interaction potential of ions with dipoles is of particular interest. At longer distances the dipole will be rotating with a statistical distribution of angles whereupon the interaction potential with an ion is attractive and has a $1/r^4$ dependence. This is longer range than the $1/r^6$ dependence for neutral species from London forces or for rotating dipole-dipole interactions. Also there are theoretical studies[22,23] showing that a $1/r^4$ dependence is sufficiently long range to yield classical behavior. We also recognize that both ion–ion and ion–dipole forces will be attenuated by the shielding effect of the ion distribution, i.e., with the Debye length. Thus we have an interesting but complex theoretical topic that deserves further investigation.

Conclusions

The electrical conductivity of the tetra-*n*-butylammonium picrate–1-chloroheptane system was examined at a temperature just above the critical temperature. At low concentrations, the conductivity data show a minimum indicative of the formation of neutral ion pairs and subsequent formation of charged clusters. The conductance increases rapidly as the concentration increases further. This corresponds to the formation of charged clusters at the expense of neutral clusters as the concentration approaches that of the critical point. The large conductance is in accordance with the suggestion of our earlier results that long-range ionic forces are important in the critical region.

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Appendix

The conductivity cell was used to measure the dielectric constant of the chloroheptane. The capacitance of the cell was measured with degassed 1-chloroheptane over the range of temperature 323–433 K. The dielectric constant is just the ratio of the capacitance with the 1-chloroheptane present to that of the evacuated cell.

The dielectric constant values for chloroheptane are listed in Table II. These data were combined with the values for lower temperatures of Watanabe and Sugiyama,[24] and eq A1 was fitted,

$$\log \epsilon = \log \epsilon(0) + At + Bt^2 \qquad \text{(A1)}$$

where ϵ is the dielectric constant, $\epsilon(0)$ the dielectric constant at 0 °C (5.909), and t the temperature in °C. The coefficients and standard deviation of the fit were $A = -1.638 \times 10^{-3}$, $B = -1.974 \times 10^{-6}$, and $\sigma = 0.033$. Our measured value at 323 K was in good agreement with that of Watanabe and Sugiyama.[24]

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